# PATENT ABSTRACTS OF JAPAN

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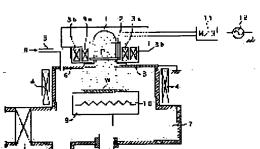
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## (54) FILM FORMING METHOD AND PLASMA DEVICE USING FOR THIS **METHOD**



(57) Abstract:

PURPOSE: To enable a ground metal film uniform in thickness to be formed on the inner wall of a fine contact hole by a method wherein a plasma CVD is carried out under conditions that a weak magnetic field or substantially a non-magnetic field is present around the substrate when a film is formed. CONSTITUTION: A helicon wave plasma generating section is equipped with a bell jar 1 which is formed of non-condcutive material so as to generate a helicon wave plasma PH inside it and two loops which turn around the bell jar 1, wherein a loop antenna 2 which couples an RF power to plasma is provided to the bell jar 1. An inner circumferential solenoid coil 3a which generates a magnetic field along the axial direction of the bell jar 1 and is primarily conducive to the propagation of helicon waves and an outer circumferential

solenoid coil 3b which generates a magnetic field along the axial direction of the bell jar 1 and is primarily conducive to the conveyance of a helicon wave plasma plasma PH are provided. By this setup, it requires no external magnetic field or only a weak external magnetic field to excite plasma.

**CLAIMS** 

[Claim(s)]

[Claim 1] The membrane formation approach of performing said plasma CVD in the membrane formation approach which forms the predetermined ingredient film on a substrate by performing plasma CVD within a high vacuum container under the conditions which make it a weak magnetic field thru/or substantial non-magnetic field near [ said ] the substrate at the time of membrane formation.

[Claim 2] Said plasma CVD is the membrane formation approach according to claim 1 performed using the helicon wave plasma.

[Claim 3] Said plasma CVD is the membrane formation approach according to claim 1 performed using inductively coupled plasma.

[Claim 4] Said predetermined ingredient film is the membrane formation approach given in any 1 term of claim 1 which is the titanium system ingredient film thru/or claim 3.

[Claim 5] The plasma equipment with which it comes to consist of said non-conductive member non-oxygen content ceramics in the plasma equipment made as [ form / by having the high-vacuum container which holds a substrate, the RF antenna arranged in the outside of the non-conductive member of said high-vacuum container which constitutes a part of internal surface at least, and a RF impression means to said RF antenna, and performing plasma CVD within said high-vacuum container / on a substrate / the predetermined ingredient film ].

[Claim 6] Said non-conductive member is plasma equipment according to claim 5 which constitutes the helicon wave plasma production chamber which goes around for said high frequency antenna and a field generation means.

[Claim 7] Said non-conductive member is plasma equipment according to claim 5 made as [ make / inductively coupled plasma / generate in this high vacuum container ] by constituting some shaft orientations of said high vacuum container.

[Claim 8] Said non-oxygen content ceramics is plasma equipment given in any 1 term of claim 5 which is silicon nitride thru/or claim 7.

## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention forms to homogeneity (Titanium Ti) system ingredient film especially used as a substrate metal membrane of the upper wiring using the so-called high density plasma, such as helicon wave plasma and inductively coupled plasma, about the plasma equipment used for the membrane formation approach and this which are applied to manufacture of a semiconductor device etc., and relates to the approach and equipment which enable reliable wiring formation. [0002]

[Description of the Prior Art] As an electrical conducting material embedding the detailed connection holes (a contact hole, beer hall, etc.) of VLSI in recent years and ULSI, metallic materials, such as aluminum (aluminum) and W (tungsten), are used widely. Moreover, in order to raise the dependability of contact by these embedding metals, generally covering the internal surface of a connection hole with the substrate metal membrane which consists of an IVa group element before embedding is performed. This substrate metal membrane expects the barrier metal to lower layer wiring, the adhesion layer to a SiOx interlayer insulation film, or the function of both these, and is prepared. As the typical configuration, the Ti/TiN cascade screen which

carried out the laminating of Ti (titanium) film and its upper layer side TiN (titanium nitride) film to the lower layer side is known.

[0003] Generally these Ti film and the TiN film are formed by the sputtering method. In addition, the spatter membrane formation process of the latter TiN film is called especially reactive sputtering from carrying out the spatter of the Ti target in a nitrogen-containing ambient atmosphere. However, it is becoming difficult to cover the high connection hole of an aspect ratio in recent years with the sputtering method with sufficient step coverage (step coverage nature). in order that the membrane formation ingredient particle begun to beat from the target may carry out incidence of this to a substrate with a certain amount of directivity, the shadowing effectiveness by the opening edge of a connection hole arises, a connection hole is deep and the particle coming flying is because it is impossible to enter until.

[0004] The CVD method which can form a barrier metal with a sufficient coverage in recent years based on the surface chemistry reaction in a connection hole from this background attracts attention. Here, about CVD membrane formation of the TiN film, it is TiCl4, for example. Various technique including the heat CVD method based on methylhydrazine reduction is known. However, the approach of enabling CVD membrane formation of Ti film is TiCl4 in the place known until now. H2 It is only an ECR-CVD method based on reduction. Ti film cannot form membranes with the usual heat CVD method because generation Gibbs energy deltaG in this system-of-reaction TiCl4+2H2 ->Ti+4HCl\*\* is as high as 209 kJ/mol (deltaG> 0) in the temperature requirement which is 100-1000 degrees C to which the usual semi-conductor process is applied.

[0005] Therefore, the approach of enabling continuation membrane formation of a Ti/TiN cascade screen is the only approach that an ECR-CVD method is known for the present condition.

[0006]

[Problem(s) to be Solved by the Invention] However, some troubles have arisen also with membrane formation of the Ti/TiN cascade screen by the ECR-CVD method for the diameter of opening of a connection hole to be reduced to 0.25 micrometers or less. The main troubles are TiCl4 for the asymmetry of the coverage of the Ti/TiN cascade screen in a connection hole and an unreacted part, or un-dissociating. It is the incorporation into a Ti/TiN cascade screen.

[0007] First, the asymmetric problem of the above-mentioned coverage is explained, referring to drawing 2 and drawing 6. Drawing 2 is SiOx by which the laminating was carried out on the lower layer wiring 21. The wafer with which opening of the connection hole 23 was carried out to the interlayer insulation film 22 is shown. Here, the chart on the left expresses near the left end of a wafer, and right-hand side drawing expresses near the right end of a wafer typically, respectively.

[0008] If above-mentioned ECR-CVD is performed about this wafer, as shown in drawing 6, thickness of the Ti film 24 formed and the TiN film 25 cannot serve as right-and-left asymmetry within each connection hole 23, and cannot form the Ti/TiN cascade screen 26 of uniform thickness. Usually, in the side-attachment-wall side of the edge approach of a wafer with much incidence of the chemical species in the plasma, the Ti/TiN cascade screen 26 is thick and is thinly formed in the side-attachment-wall side of central approach with little incidence. When extreme, the field where the Ti film 24 or the TiN film 25 is hardly formed by the side-attachment-wall side of central approach may be generated.

[0009] The main causes of this phenomenon are in the heterogeneity of a magnetic field [ / near the wafer side ]. namely, -- an ECR-CVD method -- electron cyclotron

resonance condition omega=omega c =eB/m -- [ -- however, in the angular frequency of the electron with which the angular frequency of microwave (2.45GHz) electric field and omegac perform the circular motion in omega, and e, electronic charge and m express mass of electrons, and B expresses flux density, respectively. ] In order to be satisfied, the 8.75x10-2T (875G) thing strong magnetic field is used. For this reason, the magnetic field strength near the wafer side is still higher also with the ECR plasma equipment of an emission field method in the equipment of 1x10-2T (100G) extent or the type it becomes and is high and using the plasma production room of a bell jar mold. However, it is difficult to equalize a magnetic field over the whole surface near the diameter wafer of macrostomia with a diameter of 8 inches used abundantly in recent years. And under a strong magnetic field, since the rates of capture to the magnetic field of an electron and ion differ, the charge accumulated in the substrate also does effect in the direction of incidence of ion. [0010] The asymmetry of the coverage of the Ti/TiN cascade screen 26 produced in the connection hole 23 above interior degrades the pad property in the case of embedding this connection hole 23 by the Blk-W (blanket tungsten) film which is not illustrated in a back process, and becomes the cause of making W plug producing a void. Moreover, it is SiOx in that sufficient barrier nature to the lower layer wiring 21 is not demonstrated in the thin part of the Ti/TiN cascade screen 26 \*\*\*\*. The adhesion over an interlayer insulation film 22 may fall, and the Blk-W film may exfoliate. Furthermore, since the Ti film 24 is film indispensable also when securing the ohmic nature of contact, if this Ti film 24 is not formed by sufficient thickness, the contact engine performance also has a possibility that it may be spoiled greatly. [0011] On the other hand, it is TiCl4. It is a problem relevant to the discharge dissociation effectiveness of the wallplate of plasma equipment, or the plasma undissociating [ the amount of / an unreacted part or ], it is not based on the form of plasma equipment and a certain amount of generating is not avoided. However, TiCl4 When occlusion of the unreacted part is carried out into the Ti/TiN cascade screen 26 in large quantities, chlorine is emitted by the pyrolysis in the process in which it passes through various heat treatment processes, to behind, and there is a possibility of \*\*\*\*(ing) the impurity diffusion field in Si substrate this chlorine of whose is lower layer wiring, and aluminum system wiring film, and spoiling a contact property. Moreover, when the emitted chlorine is spread along with the void and seam (contact side of the Blk-W crystal which grew from both the wall surfaces in the connection hole 23) of W plug, aluminum system wiring film is \*\*\*\*(ed), for example, and there is also a possibility formed on these W plugs of spoiling the dependability of the upper wiring. Therefore, discharge dissociation effectiveness is raised and it is TiCl4. To hold down the rate for an unreacted part and un-dissociating to the lowest possible level is desired.

[0012] Then, this invention solves an above-mentioned problem and aims at offering the plasma equipment used for the membrane formation approach and this with possible forming the substrate metal membrane of uniform thickness also inside a detailed connection hole, and possible this performing reliable wiring formation. [0013]

[Means for Solving the Problem] Since the above-mentioned purpose is attained, this invention is proposed. That is, in forming the predetermined ingredient film on a substrate by performing plasma CVD within a high vacuum container, the membrane formation approach concerning this invention performs said plasma CVD under the conditions which make it a weak magnetic field thru/or substantial non-magnetic field near [ said ] the substrate at the time of membrane formation.

[0014] This plasma CVD becomes possible by using the helicon wave plasma or inductively coupled plasma. Impress a magnetic field to the helicon wave plasma production chamber of the shape of a cylinder which consists of a non-conductive member, and impress high frequency to the loop antenna further wound around this chamber with a high frequency impression means, and accelerate this by the energy transport to the electron which led the process of Landau damping from this helicon wave, and the generation device of the helicon wave plasma makes this accelerated electron to make a helicon wave generate in this chamber, and collide with a gas molecule, and obtains a high ionization rate. At the helicon wave plasma, it is 1011-1013-/cm3 about. Although ion density can be attained, the external magnetic field used in this case is the last strong magnetic field which would be used by generation of the ECR plasma.

[0015] The generation device of one inductively coupled plasma is rotating an electron according to the electromagnetic field which supply a RF to the off-resonance antenna arranged in the outside of the non-conductive member of a high vacuum container which constitutes a part of internal surface at least from a RF impression means, and are formed inside this antenna, and is a thing of making this electron and gas molecule collide by the high probability.

[0016] The plasma generated when a non-conductive member is usually made into the cylinder configuration which makes some shaft orientations of a high vacuum container here and it considers as the multiturn antenna around which an antenna is wound by this perimeter is called ICP (Inductively Coupled Plasma). Moreover, the plasma generated when a non-conductive member is used as the top-cover part of a high vacuum container and an antenna is used as the curled form antenna installed in this bottom is called TCP (Transformer Coupled Plasma). These [ both ] are 1011-1012-/cm3. Although ion density can be attained, the external magnetic field is not used. These all can be used in this invention.

[0017] The plasma CVD of this invention uses and is suitable for membrane formation of Ti system ingredient film. as this Ti system ingredient film, there are [cascade screen / two-layer film, such as a Ti/TiN cascade screen besides each monolayer of Ti film, the TiN film, and the TiON (acid titanium nitride) film, and a Ti/TiON cascade screen, or a Ti/TiN/Ti cascade screen, / Ti/TiON/Ti ] three layer membranes further -- it is -- the combination of other arbitration of the abovementioned monolayer can be mentioned.

[0018] By the way, in this invention, the equipment with which said non-conductive member consisted of non-oxygen content ceramics is used as plasma equipment which can perform effectively membrane formation by the above-mentioned membrane formation approach. This non-conductive member is the helicon wave plasma production chamber of a bell jar mold in helicon wave plasma production equipment, is a cylinder which constitutes some shaft orientations of a high vacuum container in ICP equipment, and is the top cover of a high vacuum container in TCP equipment. These helicon wave plasma production chamber, the cylinder, and the top cover consisted of conventional common equipment using the quartz.

[0019] Here, as non-oxygen content ceramics, even if it contacts the high density plasma, spatter emission of the oxygen is not carried out, and it does not become a source of particle, but the ceramics which does not consume the chemical species in the plasma which contributes to membrane formation in large quantities can be chosen suitably. This viewpoint to silicon nitride is very suitable ceramics.

[0020]

[Function] By the membrane formation approach of this invention, since CVD is

performed using the high density plasma which does not need an external magnetic field for plasma excitation like the helicon wave plasma or inductively coupled plasma, or needs only a far low external magnetic field compared with the ECR plasma, magnetic field strength [ / near the substrate ] can be greatly reduced compared with the case of an ECR-CVD method. Consequently, the heterogeneity of a magnetic field [ / near the substrate ] is suppressed by the level which is satisfactory practically, and can cancel the asymmetry of the step coverage resulting from this. [0021] When especially this invention approach is applied to membrane formation of Ti system ingredient film used as substrate film of the upper wiring of a semiconductor device, many properties, such as the pad property of the connection hole by the upper wiring, barrier nature, and adhesion, can be improved through an improvement of the coverage of this Ti system ingredient film. Moreover, TiCl4 usually used as material gas since the plasma consistency of the above-mentioned helicon wave plasma or inductively coupled plasma is high figures double [1-] compared with it of the ECR plasma Discharge dissociation effectiveness can be improved and the ratio for un-dissociating can be reduced. Therefore, TiCl4 to the inside of Ti system ingredient film Incorporation can be controlled and the corrosion of wiring by diffusion of desorption chlorine can be prevented. [0022] Moreover, with the plasma equipment of this invention, since the nonconductive member of a high vacuum container which constitutes a part of internal surface at least, and goes around at a RF antenna is constituted using non-oxygen content ceramics, even if this non-conductive member contacts the high density plasma, spatter emission of the oxygen is not carried out. Oxygen is emitted by contact to the plasma in the quartz used conventionally, and this oxygen is Ti membrane formation system of reaction. H2 in TiCl4+2H2 ->Ti+4HCl\*\* It is TiCl4 as a result of consuming. It may have remained without being returned. Such a phenomenon is not produced in this invention. Therefore, TiCl4 to the inside of Ti system ingredient film It can become possible to control incorporation much more effectively, and the dependability of wiring formation can be raised further. [0023]

[Example] Hereafter, the concrete example of this invention is explained. [0024] Example 1 this example is an example which constituted the bell jar which is the helicon wave plasma production chamber of helicon wave plasma-CVD equipment using silicon nitride. The notional configuration of this CVD system is shown in <u>drawing 1</u>. First, the helicon wave plasma production section is the helicon wave plasma PH to the interior. It has the bell jar 1 which consists of a non-conductive ingredient for making it generate, and two loop formations which go this bell jar 1 around. It is prepared so that the loop antenna 2 for carrying out coupling of the RF power to the plasma and the above-mentioned chamber 1 may be gone around. inner circumference side solenoid coil 3a which is made to generate the field in alignment with the shaft orientations of this chamber 1, and contributes mainly to propagation of a helicon wave -- and -- mainly -- helicon wave plasma PH Let periphery side solenoid coil 3b which contributes to transportation be the main components.

[0025] Here, the component of the above-mentioned bell jar 1 is silicon nitride. In this CVD system, even if the helicon wave plasma of high density generates inside, spatter emission of the oxygen is not carried out from the container wall of a bell jar 1 by this configuration.

[0026] RF power is impressed to the above-mentioned loop antenna 2 through the matching network (M/N) 11 for impedance matching from the RF power source 12

for plasma excitation, and the current of the direction of the circumference of reverse flows mutually to the loop formation of two upper and lower sides. Here, the frequency of the above-mentioned RF power source 12 for plasma excitation was set to 13.56MHz. In addition, the distance between both loop formations is optimized according to the wave number of a desired helicon wave.

[0027] It connects with the process chamber 7, the emission field which the abovementioned inner circumference side solenoid coil 3a and periphery side solenoid coil 3b form is met, and the above-mentioned bell jar 1 is the helicon wave plasma PH to the interior of this process chamber 7. It is made as [ pull ]. The side-attachment-wall side and base of the process chamber 7 are constituted using conductive ingredients, such as stainless steel. The interior receives supply of required gas in CVD from the gas supply line 5 in which high vacuum exhaust air is carried out in the direction of arrow-head A through the exhaust hole 8 by the exhaust system which is not illustrated and by which opening is carried out to the upside top plate 6 in the direction of arrow-head B, and is connected to the load lock chamber which is not further illustrated through a gate valve 13 in the side-attachment-wall side. [0028] The conductive substrate stage 9 electrically insulated from that wall surface is held in the interior of the above-mentioned process chamber 7, and it is made as [ perform / hold for example, the wafer W as a processed substrate, and / on this, / predetermined CVD ]. The heater 10 for heating the wafer W in a process to desired temperature is laid under the above-mentioned substrate stage 9.

[0029] In addition, although not illustrated, it is in during membrane formation. RF power source for bias impression may be connected to the leg of the above-mentioned substrate stage 9 through a matching network if needed to perform flattening of the situ film. Furthermore, in order to complete the emission field in the about nine above-mentioned substrate stage, the magnet 4 which can generate a multi-cusp field as an auxiliary field generation means is arranged in the exterior of the above-mentioned process chamber 7.

[0030] In example 2 this example, the helicon wave plasma-CVD equipment stated in the example 1 is used, and it is SiOx. The Ti/TiN cascade screen was formed so that the connection hole by which opening was carried out to the interlayer insulation film might be covered, and the upper wiring was further formed on this. This process is explained referring to drawing 2 thru/or drawing 4.

[0031] The important section cross section of the wafer used as a CVD sample of this example is shown in <u>drawing 2</u>. This wafer is SiOx on the lower layer wiring 21. The laminating of the interlayer insulation film 22 is carried out, and it is this SiOx. It is the thing of the phase which carried out opening of the connection hole 23 with an open aperture of about 0.25 micrometers to the interlayer insulation film 22, and the chart on the left expresses near the left end of a wafer, and right-hand side drawing expresses near the right end of a wafer typically, respectively.

[0032] Here, even if the above-mentioned lower layer wiring 21 is the impurity diffused layer formed for example, into Si substrate, it may be wiring film which consists of polish recon, aluminum system ingredient, a refractory metal, silicide, etc. [0033] This wafer was set in the above-mentioned CVD system, and continuation membrane formation of the Ti film 24 with a thickness of about 30nm and the TiN film 25 with a thickness of about 70nm was carried out on condition that the following as an example.

[Ti film 24 membrane-formation conditions]

TiCl4 Flow rate 20 SCCMH2 Flow rate 40 SCCM gas pressure 0.05 Pa source power (PH excitation) 2.5 kW (13.56MHz)

Stage temperature 420 \*\* [TiN film 25 membrane-formation conditions] TiCl4 Flow rate 20 SCCMH2 Flow rate 26 SCCMN2 Flow rate 6 SCCMAr flow rate 75 SCCM gas pressure 0.1 Pa source power (PH excitation) 2.5 kW (13.56MHz) Stage temperature 420 \*\* [0034] Within this CVD system, since magnetic field strength [ / near the front face of Wafer W] was very low, as shown in drawing 3, the Ti film 24 and the TiN film 25 were formed in respectively uniform thickness. Consequently, the internal surface of the connection hole 23 was covered with the Ti/TiN cascade screen 26 of uniform thickness. At this time, it is TiCl4 by the high discharge dissociation effectiveness of the helicon wave plasma. Since it is small and oxygen is not emitted from a bell jar 1, a part for un-dissociating is H2. The reduction reaction to depend was not checked, either.

[0035] Then, as shown in drawing 4, contact to the lower layer wiring 21 was completed by performing etchback of the Blk-W film formed according to the conventional method, and the above-mentioned Ti/TiN cascade screen 26, forming the W plug 27 and performing on this patterning of the upper wiring 28 which consists of aluminum system wiring film etc. At this time, since the coverage of the Ti/TiN cascade screen 26 of a substrate is good, the void has not been produced to the

above-mentioned W plug 27.

[0036] Although the inside of this process of a series of and Wafer W are heated at the time of front [exposure] baking of the resist film at the time of performing patterning of the time of membrane formation of aluminum system wiring film, and the upper wiring 28 at the time of membrane formation of the Blk-W film, and after [ exposure ] baking, it is TiCl4 unreacted to the Ti/TiN cascade screen 26 as mentioned above. Since it was hardly incorporated, the corrosion of wiring like before was not observed at all.

[0037] Example 3 this example is an example of the ICP-CVD system which constituted the cylinder for inductively-coupled-plasma generation from silicon nitride. The notional configuration of this ICP-CVD system is shown in drawing 5. In this equipment, a part of side-attachment-wall side of the process chamber 32 is used as the cylinder 33 which consists of silicon nitride, and parts 31 other than this, i.e., a top cover, a lower side-attachment-wall side, a base, etc. consist of conductive ingredients, such as stainless steel.

[0038] The multiturn antenna 37 is wound around the periphery side of the abovementioned cylinder 33. A RF is impressed to this multiturn antenna 37 through a matching network (M/N) 38 from the RF power source 39 for plasma excitation. Here, the frequency of the above-mentioned RF power source 39 for plasma excitation was set to 2MHz.

[0039] High vacuum exhaust air is carried out in the direction of arrow-head D through the exhaust hole 34 by the exhaust system which is not illustrated, and the interior of the above-mentioned process chamber 32 is made by CVD as [ receive / supply of required gas ] in the direction of arrow-head C from the gas supply line 36 by which opening is carried out to a base. The process chamber 32 has held the conductive substrate stage 35 electrically insulated from that wall surface again, holds for example, the wafer W as a processed substrate on this, and is the inductive discharge plasma PI. It is made as [ perform / make it generate and / predetermined CVD].

[0040] The heater 40 for heating the wafer W in a process to desired temperature is laid under the above-mentioned substrate stage 35. In addition, although not illustrated, RF power source for bias impression may be connected to the abovementioned substrate stage 35 through a matching network if needed to perform

flattening of the film insitu during membrane formation.

[0041] In example 4 this example, the ICP-CVD system stated in the example 3 is used, and it is SiOx. The Ti/TiN cascade screen which covers the connection hole by which opening was carried out to the interlayer insulation film was formed. The wafer used as a CVD sample of this example is the same as what was mentioned above in the example 2. This wafer was set in the above-mentioned ICP-CVD system, and continuation membrane formation of the Ti film 24 and the TiN film 25 was carried out on condition that the following as an example.

[Ti film 24 membrane-formation conditions]

TiCl4 Flow rate 20 SCCMH2 Flow rate 40 SCCM gas pressure 0.1 Pa source power (PI excitation) 3 kW (2 MHz)

Stage temperature 420 \*\* [TiN film 25 membrane-formation conditions]
TiCl4 Flow rate 20 SCCMH2 Flow rate 26 SCCMN2 Flow rate 6 SCCMAr flow rate
75 SCCM gas pressure 0.2 Pa source power (PI excitation) 3 kW (2 MHz)
Stage temperature 420 \*\* [0042] Within the ICP-CVD system, since magnetic field
strength [ / near the front face of Wafer W ] was zero mostly, it was able to form the
conformal Ti film 24 and the TiN film 25. Moreover, also after forming the W plug
27 and the upper wiring 28 through a series of back processes, the corrosion of wiring
was not observed at all. As mentioned above, although this invention was explained
based on the example of four examples, this invention is not limited to these examples.
at all, and the configuration of a CVD system, the configuration of a sample wafer,
the details of CVD conditions, etc. can be changed suitably.

[0043]

[Effect of the Invention] TiCl4 of the asymmetry of the coverage which originates CVD of Ti system ingredient film using the high density plasma in the heterogeneity of the magnetic field near the substrate if this invention is applied so that clearly also from the above explanation, or unreacted and un-dissociating It can carry out preventing the corrosion of the upper wiring and lower layer wiring by incorporation of the residue. Thereby, many properties, such as the pad property of the connection hole by the upper wiring, barrier nature, and adhesion, are improvable.

[0044] And helicon wave plasma equipment and inductively-coupled-plasma equipment which are used in this invention have a simple configuration configuration, and only its part which requires neither the source of microwave nor an expensive large-sized solenoid coil compared with conventional ECR plasma equipment is advantageous to a miniaturization and low-cost-izing. This invention contributes to high integration of a semiconductor device, high-performance-izing, and high reliance-ization greatly through a raise in reliance of detailed wiring formation.

## TECHNICAL FIELD

[Industrial Application] This invention forms to homogeneity (Titanium Ti) system ingredient film especially used as a substrate metal membrane of the upper wiring using the so-called high density plasma, such as helicon wave plasma and inductively coupled plasma, about the plasma equipment used for the membrane formation approach and this which are applied to manufacture of a semiconductor device etc., and relates to the approach and equipment which enable reliable wiring formation.

#### PRIOR ART

[Description of the Prior Art] As an electrical conducting material embedding the detailed connection holes (a contact hole, beer hall, etc.) of VLSI in recent years and ULSI, metallic materials, such as aluminum (aluminum) and W (tungsten), are used widely. Moreover, in order to raise the dependability of contact by these embedding metals, generally covering the internal surface of a connection hole with the substrate metal membrane which consists of an IVa group element before embedding is performed. This substrate metal membrane expects the barrier metal to lower layer wiring, the adhesion layer to a SiOx interlayer insulation film, or the function of both these, and is prepared. As the typical configuration, the Ti/TiN cascade screen which carried out the laminating of Ti (titanium) film and its upper layer side TiN (titanium nitride) film to the lower layer side is known.

[0003] Generally these Ti film and the TiN film are formed by the sputtering method. In addition, the spatter membrane formation process of the latter TiN film is called especially reactive sputtering from carrying out the spatter of the Ti target in a nitrogen-containing ambient atmosphere. However, it is becoming difficult to cover the high connection hole of an aspect ratio in recent years with the sputtering method with sufficient step coverage (step coverage nature). in order that the membrane formation ingredient particle begun to beat from the target may carry out incidence of this to a substrate with a certain amount of directivity, the shadowing effectiveness by the opening edge of a connection hole arises, a connection hole is deep and the particle coming flying is because it is impossible to enter until.

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[0005] Therefore, the approach of enabling continuation membrane formation of a Ti/TiN cascade screen is the only approach that an ECR-CVD method is known for the present condition.

#### EFFECT OF THE INVENTION

[Effect of the Invention] TiCl4 of the asymmetry of the coverage which originates CVD of Ti system ingredient film using the high density plasma in the heterogeneity of the magnetic field near the substrate if this invention is applied so that clearly also from the above explanation, or unreacted and un-dissociating It can carry out preventing the corrosion of the upper wiring and lower layer wiring by incorporation of the residue. Thereby, many properties, such as the pad property of the connection hole by the upper wiring, barrier nature, and adhesion, are improvable.

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large-sized solenoid coil compared with conventional ECR plasma equipment is advantageous to a miniaturization and low-cost-izing. This invention contributes to high integration of a semiconductor device, high-performance-izing, and high reliance-ization greatly through a raise in reliance of detailed wiring formation.

## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, some troubles have arisen also with membrane formation of the Ti/TiN cascade screen by the ECR-CVD method for the diameter of opening of a connection hole to be reduced to 0.25 micrometers or less. The main troubles are TiCl4 for the asymmetry of the coverage of the Ti/TiN cascade screen in a connection hole and an unreacted part, or un-dissociating. It is the incorporation into a Ti/TiN cascade screen.

[0007] First, the asymmetric problem of the above-mentioned coverage is explained, referring to drawing 2 and drawing 6. Drawing 2 is SiOx by which the laminating was carried out on the lower layer wiring 21. The wafer with which opening of the connection hole 23 was carried out to the interlayer insulation film 22 is shown. Here, the chart on the left expresses near the left end of a wafer, and right-hand side drawing expresses near the right end of a wafer typically, respectively. [0008] If above-mentioned ECR-CVD is performed about this wafer, as shown in drawing 6, thickness of the Ti film 24 formed and the TiN film 25 cannot serve as right-and-left asymmetry within each connection hole 23, and cannot form the Ti/TiN cascade screen 26 of uniform thickness. Usually, in the side-attachment-wall side of the edge approach of a wafer with much incidence of the chemical species in the plasma, the Ti/TiN cascade screen 26 is thick and is thinly formed in the sideattachment-wall side of central approach with little incidence. When extreme, the field where the Ti film 24 or the TiN film 25 is hardly formed by the side-attachment-

wall side of central approach may be generated.

[0009] The main causes of this phenomenon are in the heterogeneity of a magnetic field [ / near the wafer side ]. namely, -- an ECR-CVD method -- electron cyclotron resonance condition omega=omega c =eB/m -- [ -- however, in the angular frequency of the electron with which the angular frequency of microwave (2.45GHz) electric field and omegac perform the circular motion in omega, and e, electronic charge and m express mass of electrons, and B expresses flux density, respectively. ] In order to be satisfied, the 8.75x10-2T (875G) thing strong magnetic field is used. For this reason, the magnetic field strength near the wafer side is still higher also with the ECR plasma equipment of an emission field method in the equipment of 1x10-2T (100G) extent or the type it becomes and is high and using the plasma production room of a bell jar mold. However, it is difficult to equalize a magnetic field over the whole surface near the diameter wafer of macrostomia with a diameter of 8 inches used abundantly in recent years. And under a strong magnetic field, since the rates of capture to the magnetic field of an electron and ion differ, the charge accumulated in the substrate also does effect in the direction of incidence of ion.

[0010] The asymmetry of the coverage of the Ti/TiN cascade screen 26 produced in the connection hole 23 above interior degrades the pad property in the case of embedding this connection hole 23 by the Blk-W (blanket tungsten) film which is not illustrated in a back process, and becomes the cause of making W plug producing a void. Moreover, it is SiOx in that sufficient barrier nature to the lower layer wiring 21 is not demonstrated in the thin part of the Ti/TiN cascade screen 26 \*\*\*\*. The

adhesion over an interlayer insulation film 22 may fall, and the Blk-W film may exfoliate. Furthermore, since the Ti film 24 is film indispensable also when securing the ohmic nature of contact, if this Ti film 24 is not formed by sufficient thickness, the contact engine performance also has a possibility that it may be spoiled greatly. [0011] On the other hand, it is TiCl4. It is a problem relevant to the discharge dissociation effectiveness of the wallplate of plasma equipment, or the plasma undissociating [ the amount of / an unreacted part or ], it is not based on the form of plasma equipment and a certain amount of generating is not avoided. However, TiCl4 When occlusion of the unreacted part is carried out into the Ti/TiN cascade screen 26 in large quantities, chlorine is emitted by the pyrolysis in the process in which it passes through various heat treatment processes, to behind, and there is a possibility of \*\*\*\*(ing) the impurity diffusion field in Si substrate this chlorine of whose is lower layer wiring, and aluminum system wiring film, and spoiling a contact property. Moreover, when the emitted chlorine is spread along with the void and seam (contact side of the Blk-W crystal which grew from both the wall surfaces in the connection hole 23) of W plug, aluminum system wiring film is \*\*\*\*(ed), for example, and there is also a possibility formed on these W plugs of spoiling the dependability of the upper wiring. Therefore, discharge dissociation effectiveness is raised and it is TiCl4. To hold down the rate for an unreacted part and un-dissociating to the lowest possible level is desired.

[0012] Then, this invention solves an above-mentioned problem and aims at offering the plasma equipment used for the membrane formation approach and this with possible forming the substrate metal membrane of uniform thickness also inside a detailed connection hole, and possible this performing reliable wiring formation.

#### **MEANS**

[Means for Solving the Problem] Since the above-mentioned purpose is attained, this invention is proposed. That is, in forming the predetermined ingredient film on a substrate by performing plasma CVD within a high vacuum container, the membrane formation approach concerning this invention performs said plasma CVD under the conditions which make it a weak magnetic field thru/or substantial non-magnetic field near [ said ] the substrate at the time of membrane formation.

[0014] This plasma CVD becomes possible by using the helicon wave plasma or inductively coupled plasma. Impress a magnetic field to the helicon wave plasma production chamber of the shape of a cylinder which consists of a non-conductive member, and impress high frequency to the loop antenna further wound around this chamber with a high frequency impression means, and accelerate this by the energy transport to the electron which led the process of Landau damping from this helicon wave, and the generation device of the helicon wave plasma makes this accelerated electron to make a helicon wave generate in this chamber, and collide with a gas molecule, and obtains a high ionization rate. At the helicon wave plasma, it is 1011-1013-/cm3 about. Although ion density can be attained, the external magnetic field used in this case is the last strong magnetic field which would be used by generation of the ECR plasma.

[0015] The generation device of one inductively coupled plasma is rotating an electron according to the electromagnetic field which supply a RF to the off-resonance antenna arranged in the outside of the non-conductive member of a high vacuum container which constitutes a part of internal surface at least from a RF

impression means, and are formed inside this antenna, and is a thing of making this electron and gas molecule collide by the high probability.

[0016] The plasma generated when a non-conductive member is usually made into the cylinder configuration which makes some shaft orientations of a high vacuum container here and it considers as the multiturn antenna around which an antenna is wound by this perimeter is called ICP (Inductively Coupled Plasma). Moreover, the plasma generated when a non-conductive member is used as the top-cover part of a high vacuum container and an antenna is used as the curled form antenna installed in this bottom is called TCP (Transformer Coupled Plasma). These [both] are 1011-1012-/cm3. Although ion density can be attained, the external magnetic field is not used. These all can be used in this invention.

[0017] The plasma CVD of this invention uses and is suitable for membrane formation of Ti system ingredient film. as this Ti system ingredient film, there are [cascade screen / two-layer film, such as a Ti/TiN cascade screen besides each monolayer of Ti film, the TiN film, and the TiON (acid titanium nitride) film, and a Ti/TiON cascade screen, or a Ti/TiN/Ti cascade screen, / Ti/TiON/Ti ] three layer membranes further -- it is -- the combination of other arbitration of the abovementioned monolayer can be mentioned.

[0018] By the way, in this invention, the equipment with which said non-conductive member consisted of non-oxygen content ceramics is used as plasma equipment which can perform effectively membrane formation by the above-mentioned membrane formation approach. This non-conductive member is the helicon wave plasma production chamber of a bell jar mold in helicon wave plasma production equipment, is a cylinder which constitutes some shaft orientations of a high vacuum container in ICP equipment, and is the top cover of a high vacuum container in TCP equipment. These helicon wave plasma production chamber, the cylinder, and the top cover consisted of conventional common equipment using the quartz.

[0019] Here, as non-oxygen content ceramics, even if it contacts the high density plasma, spatter emission of the oxygen is not carried out, and it does not become a source of particle, but the ceramics which does not consume the chemical species in the plasma which contributes to membrane formation in large quantities can be chosen suitably. This viewpoint to silicon nitride is very suitable ceramics.

#### **OPERATION**

[Function] By the membrane formation approach of this invention, since CVD is performed using the high density plasma which does not need an external magnetic field for plasma excitation like the helicon wave plasma or inductively coupled plasma, or needs only a far low external magnetic field compared with the ECR plasma, magnetic field strength [/ near the substrate] can be greatly reduced compared with the case of an ECR-CVD method. Consequently, the heterogeneity of a magnetic field [/ near the substrate] is suppressed by the level which is satisfactory practically, and can cancel the asymmetry of the step coverage resulting from this. [0021] When especially this invention approach is applied to membrane formation of Ti system ingredient film used as substrate film of the upper wiring of a semiconductor device, many properties, such as the pad property of the connection hole by the upper wiring, barrier nature, and adhesion, can be improved through an improvement of the coverage of this Ti system ingredient film. Moreover, TiCl4 usually used as material gas since the plasma consistency of the above-mentioned

helicon wave plasma or inductively coupled plasma is high figures double [1-] compared with it of the ECR plasma Discharge dissociation effectiveness can be improved and the ratio for un-dissociating can be reduced. Therefore, TiCl4 to the inside of Ti system ingredient film Incorporation can be controlled and the corrosion of wiring by diffusion of desorption chlorine can be prevented. [0022] Moreover, with the plasma equipment of this invention, since the nonconductive member of a high vacuum container which constitutes a part of internal surface at least, and goes around at a RF antenna is constituted using non-oxygen content ceramics, even if this non-conductive member contacts the high density plasma, spatter emission of the oxygen is not carried out. Oxygen is emitted by contact to the plasma in the quartz used conventionally, and this oxygen is Ti membrane formation system of reaction. H2 in TiCl4+2H2 ->Ti+4HCl\*\* It is TiCl4 as a result of consuming. It may have remained without being returned. Such a phenomenon is not produced in this invention. Therefore, TiCl4 to the inside of Ti system ingredient film It can become possible to control incorporation much more effectively, and the dependability of wiring formation can be raised further.

#### **EXAMPLE**

[Example] Hereafter, the concrete example of this invention is explained. [0024] Example 1 this example is an example which constituted the bell jar which is the helicon wave plasma production chamber of helicon wave plasma-CVD equipment using silicon nitride. The notional configuration of this CVD system is shown in drawing 1. First, the helicon wave plasma production section is the helicon wave plasma PH to the interior. It has the bell jar 1 which consists of a non-conductive ingredient for making it generate, and two loop formations which go this bell jar 1 around. It is prepared so that the loop antenna 2 for carrying out coupling of the RF power to the plasma and the above-mentioned chamber 1 may be gone around. inner circumference side solenoid coil 3a which is made to generate the field in alignment with the shaft orientations of this chamber 1, and contributes mainly to propagation of a helicon wave -- and -- mainly -- helicon wave plasma PH Let periphery side solenoid coil 3b which contributes to transportation be the main components.

[0025] Here, the component of the above-mentioned bell jar 1 is silicon nitride. In this CVD system, even if the helicon wave plasma of high density generates inside, spatter emission of the oxygen is not carried out from the container wall of a bell jar 1 by this configuration.

[0026] RF power is impressed to the above-mentioned loop antenna 2 through the matching network (M/N) 11 for impedance matching from the RF power source 12 for plasma excitation, and the current of the direction of the circumference of reverse flows mutually to the loop formation of two upper and lower sides. Here, the frequency of the above-mentioned RF power source 12 for plasma excitation was set to 13.56MHz. In addition, the distance between both loop formations is optimized according to the wave number of a desired helicon wave.

[0027] It connects with the process chamber 7, the emission field which the above-mentioned inner circumference side solenoid coil 3a and periphery side solenoid coil 3b form is met, and the above-mentioned bell jar 1 is the helicon wave plasma PH to the interior of this process chamber 7. It is made as [pull]. The side-attachment-wall side and base of the process chamber 7 are constituted using conductive ingredients,

such as stainless steel. The interior receives supply of required gas in CVD from the gas supply line 5 in which high vacuum exhaust air is carried out in the direction of arrow-head A through the exhaust hole 8 by the exhaust system which is not illustrated and by which opening is carried out to the upside top plate 6 in the direction of arrow-head B, and is connected to the load lock chamber which is not further illustrated through a gate valve 13 in the side-attachment-wall side.

[0028] The conductive substrate stage 9 electrically insulated from that wall surface is held in the interior of the above-mentioned process chamber 7, and it is made as [perform / hold for example, the wafer W as a processed substrate, and / on this, / predetermined CVD]. The heater 10 for heating the wafer W in a process to desired temperature is laid under the above-mentioned substrate stage 9.

[0029] In addition, although not illustrated, it is in during membrane formation. RF power source for bias impression may be connected to the leg of the above-mentioned substrate stage 9 through a matching network if needed to perform flattening of the situ film. Furthermore, in order to complete the emission field in the about nine above-mentioned substrate stage, the magnet 4 which can generate a multi-cusp field as an auxiliary field generation means is arranged in the exterior of the above-mentioned process chamber 7.

[0030] In example 2 this example, the helicon wave plasma-CVD equipment stated in the example 1 is used, and it is SiOx. The Ti/TiN cascade screen was formed so that the connection hole by which opening was carried out to the interlayer insulation film might be covered, and the upper wiring was further formed on this. This process is explained referring to drawing 2 thru/or drawing 4.

[0031] The important section cross section of the wafer used as a CVD sample of this example is shown in <u>drawing 2</u>. This wafer is SiOx on the lower layer wiring 21. The laminating of the interlayer insulation film 22 is carried out, and it is this SiOx. It is the thing of the phase which carried out opening of the connection hole 23 with an open aperture of about 0.25 micrometers to the interlayer insulation film 22, and the chart on the left expresses near the left end of a wafer, and right-hand side drawing expresses near the right end of a wafer typically, respectively.

[0032] Here, even if the above-mentioned lower layer wiring 21 is the impurity diffused layer formed for example, into Si substrate, it may be wiring film which consists of polish recon, aluminum system ingredient, a refractory metal, silicide, etc. [0033] This wafer was set in the above-mentioned CVD system, and continuation membrane formation of the Ti film 24 with a thickness of about 30nm and the TiN film 25 with a thickness of about 70nm was carried out on condition that the following as an example.

[Ti film 24 membrane-formation conditions]

TiCl4 Flow rate 20 SCCMH2 Flow rate 40 SCCM gas pressure 0.05 Pa source power (PH excitation) 2.5 kW (13.56MHz)

Stage temperature 420 \*\* [TiN film 25 membrane-formation conditions] TiCl4 Flow rate 20 SCCMH2 Flow rate 26 SCCMN2 Flow rate 6 SCCMAr flow rate 75 SCCM gas pressure 0.1 Pa source power (PH excitation) 2.5 kW (13.56MHz) Stage temperature 420 \*\* [0034] Within this CVD system, since magnetic field strength [ / near the front face of Wafer W ] was very low, as shown in drawing 3, the Ti film 24 and the TiN film 25 were formed in respectively uniform thickness. Consequently, the internal surface of the connection hole 23 was covered with the Ti/TiN cascade screen 26 of uniform thickness. At this time, it is TiCl4 by the high discharge dissociation effectiveness of the helicon wave plasma. Since it is small and oxygen is not emitted from a bell jar 1, a part for un-dissociating is H2. The reduction

reaction to depend was not checked, either.

[0035] Then, as shown in drawing 4, contact to the lower layer wiring 21 was completed by performing etchback of the Blk-W film formed according to the conventional method, and the above-mentioned Ti/TiN cascade screen 26, forming the W plug 27 and performing on this patterning of the upper wiring 28 which consists of aluminum system wiring film etc. At this time, since the coverage of the Ti/TiN cascade screen 26 of a substrate is good, the void has not been produced to the above-mentioned W plug 27.

[0036] Although the inside of this process of a series of and Wafer W are heated at the time of front [exposure] baking of the resist film at the time of performing patterning of the time of membrane formation of aluminum system wiring film, and the upper wiring 28 at the time of membrane formation of the Blk-W film, and after [exposure] baking, it is TiCl4 unreacted to the Ti/TiN cascade screen 26 as mentioned above. Since it was hardly incorporated, the corrosion of wiring like before was not observed at all.

[0037] Example 3 this example is an example of the ICP-CVD system which constituted the cylinder for inductively-coupled-plasma generation from silicon nitride. The notional configuration of this ICP-CVD system is shown in <u>drawing 5</u>. In this equipment, a part of side-attachment-wall side of the process chamber 32 is used as the cylinder 33 which consists of silicon nitride, and parts 31 other than this, i.e., a top cover, a lower side-attachment-wall side, a base, etc. consist of conductive ingredients, such as stainless steel.

[0038] The multiturn antenna 37 is wound around the periphery side of the above-mentioned cylinder 33. A RF is impressed to this multiturn antenna 37 through a matching network (M/N) 38 from the RF power source 39 for plasma excitation. Here, the frequency of the above-mentioned RF power source 39 for plasma excitation was set to 2MHz.

[0039] High vacuum exhaust air is carried out in the direction of arrow-head D through the exhaust hole 34 by the exhaust system which is not illustrated, and the interior of the above-mentioned process chamber 32 is made by CVD as [receive / supply of required gas] in the direction of arrow-head C from the gas supply line 36 by which opening is carried out to a base. The process chamber 32 has held the conductive substrate stage 35 electrically insulated from that wall surface again, holds for example, the wafer W as a processed substrate on this, and is the inductive discharge plasma PI. It is made as [perform / make it generate and / predetermined CVD].

[0040] The heater 40 for heating the wafer W in a process to desired temperature is laid under the above-mentioned substrate stage 35. In addition, although not illustrated, RF power source for bias impression may be connected to the above-mentioned substrate stage 35 through a matching network if needed to perform flattening of the film insitu during membrane formation.

[0041] In example 4 this example, the ICP-CVD system stated in the example 3 is used, and it is SiOx. The Ti/TiN cascade screen which covers the connection hole by which opening was carried out to the interlayer insulation film was formed. The wafer used as a CVD sample of this example is the same as what was mentioned above in the example 2. This wafer was set in the above-mentioned ICP-CVD system, and continuation membrane formation of the Ti film 24 and the TiN film 25 was carried out on condition that the following as an example.

[Ti film 24 membrane-formation conditions]

TiCl4 Flow rate 20 SCCMH2 Flow rate 40 SCCM gas pressure 0.1 Pa source power

(PI excitation) 3 kW (2 MHz)

Stage temperature 420 \*\* [TiN film 25 membrane-formation conditions] TiCl4 Flow rate 20 SCCMH2 Flow rate 26 SCCMN2 Flow rate 6 SCCMAr flow rate 75 SCCM gas pressure 0.2 Pa source power (PI excitation) 3 kW (2 MHz) Stage temperature 420 \*\* [0042] Within the ICP-CVD system, since magnetic field strength [ / near the front face of Wafer W ] was zero mostly, it was able to form the conformal Ti film 24 and the TiN film 25. Moreover, also after forming the W plug 27 and the upper wiring 28 through a series of back processes, the corrosion of wiring was not observed at all. As mentioned above, although this invention was explained based on the example of four examples, this invention is not limited to these examples at all, and the configuration of a CVD system, the configuration of a sample wafer, the details of CVD conditions, etc. can be changed suitably.

## **DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

[Drawing 1] It is the outline sectional view showing the example of 1 configuration of the helicon wave plasma-CVD equipment which applied this invention.

[Drawing 2] In the process which applied this invention to CVD of a Ti/TiN cascade screen, it is the typical sectional view showing the condition of a sample wafer.

[Drawing 3] The connection hole of <u>drawing 2</u> is the typical sectional view showing the condition of having been covered with the Ti/TiN cascade screen.

[Drawing 4] It is the typical sectional view showing the condition that the connection hole of drawing 3 was embedded with W plug, and the upper wiring was formed further.

[Drawing 5] It is the outline sectional view showing the example of 1 configuration of the ICP-CVD system which applied this invention.

[Drawing 6] In the conventional ECR-CVD, it is the typical sectional view showing the condition that the coverage of a Ti/TiN cascade screen became unsymmetrical inside the connection hole.

[Description of Notations]

1 Bell Jar

2 Loop Antenna

3a Inner circumference side solenoid coil

3b Periphery side solenoid coil

7 32 Process chamber

9 35 Substrate stage

10 40 Heater

12 39 RF power source for plasma excitation

22 SiOx Interlayer Insulation Film

23 Connection Hole

24 Ti Film

25 TiN Film

26 Ti/TiN Cascade Screen

33 Cylinder

37 Multiturn Antenna

W Wafer

PH Helicon wave plasma

PI Inductively coupled plasma